SPECTROSCOPIC AND ELECTRONIC PARAMETERS OF LAYERED FERROELECTRIC HIGH-*k* TITANATE $Pr_2Ti_2O_7$

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Rare-earth dititanates $Ln_2Ti_2O_7$ (Ln = La, Ce, Pr, Nd) with a low-symmetry crystal structure in polar space group $P2_1$ possess interesting ferroelectric, nonlinear optical, dielectric and photocatalytic properties. The properties of $Pr_2Ti_2O_7$ (PTO), however, are less studied and should be completed. The present study is aimed at a synthesis of a high quality sample of PTO and evaluation of micromorphplogy, spectroscopic parameters and electronic structure of this intrigue titanate.

A powder sample of PTO was prepared by solid state synthesis from a stoichiometric mixture of high purity simple oxides. As starting reagents, Pr_6O_{11} (99.9%) and TiO_2 (99.99%) were used. After grinding in an agate mortar, the mixture with PTO stoichiometry was calcined at 850°C for 60h and then reacted at 1100°C for a total time of 300h (60h + 90h + 150h) with intermediate grinding steps. The last heat treatment was performed without compaction, resulting in loosely agglomerated powders. XRD patterns were recorded after each heat treatment with a STOE diffractometer using Cu Kα radiation. Cell parameter calculations were performed by the least square fit method. Micromorphology of the PTO crystals was observed by scanning electron microscopy (SEM) with the help of LEO 1430 device. Infrared (IR) spectra were recorded over the range of 500-1500 cm^{-1} using INFRALUM FT-801 (LUMEX, Russia) spectrometer with a spectral resolution of 1 cm^{-1}. Samples for IR measurements were prepared by pressing 1 mg of the material into a 500-mg, 1 mm-thick KBr pellet. Raman spectrum of the PTO powder was measured using RFS-100s spectrometer (Bruker) over the spectral range of 0–1000 cm^{-1} at the spectral resolution of 1 cm^{-1}. The observation of electronic parameters of PTO was produced using surface analysis center SSC (Riber) with XPS method. The PTO powder is formed by uniform roundish coalescent grains of ~1 μm in diameter. There are no facetted grains and this indicates that recrystallization temperature of PTO is far above the temperature of T = 1100°C. The XRD curve is completely indexed in relation to the known PTO structural parameters. IR spectrum of as-prepared PTO crystals over 500-1500 cm^{-1} spectral region have been measured. An appropriate relation is found between earlier experimental results and those measured in the present study. Raman spectrum recorded for PTO crystals contains a lot of sharp lines and individual Raman lines (82 – 154 cm^{-1}) are very narrow with as low FWHM as ~5 cm^{-1}. All the spectral features recorded by XPS are attributed to the constituent element core levels or Auger lines. The relative element contents were estimated by the Pr $3d_{5/2}$, Ti $2p_{3/2}$ lines and the components of the O 1s peak at 529.6 and 527.1 eV [16]. The results of calculations Pr:Ti:O = 0.18:0.16:0.66 are in good agreement with the nominal composition Pr:Ti:O = 0.18:0.18:0.64. The Auger parameters of titanium and oxygen ions in PTO are α_{Ti} = 872.8 and α_O = 1042.3 eV and are in good relation to those in $Nd_2Ti_2O_7$ and $La_2Ti_2O_7$.